

Electron correlation induced transverse delocalization and longitudinal confinement in excited states of phenyl-substituted polyacetylenes

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Electron-electron interactions in general lead to both ground state and excited state confinement. We show, however, that in phenyl-substituted polyacetylenes electron-electron interactions cause enhanced delocalization of quasiparticles in the optically excited state from the backbone polyene chain into the phenyl groups, which in turn leads to enhanced confinement in the chain direction. This co-operative delocalization-confinement lowers the energy of the one-photon state and raises the relative energy of the lowest two-photon state. The two-photon state is slightly below the optical state in mono-phenyl substituted polyacetylenes, but above the optical state in di-phenyl substituted polyacetylenes, thereby explaining the strong photoluminescence of the latter class of materials. We present a detailed mechanism of the crossover in the energies of the one- and two-photon states in these systems. In addition, we calculate the optical absorption spectra over a wide wavelength region, and make specific predictions for the polarizations of low and high energy transitions that can be tested on oriented samples. Within existing theories of light emission from π -conjugated polymers, strong photoluminescence should be restricted to materials whose optical gaps are larger than that of trans-polyacetylene. The present work shows that conceptually at least, it is possible to have light emission from systems with smaller optical gaps.

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I. INTRODUCTION

The absence of photoluminescence (PL) in linear polyenes, trans-polyacetylene (t-PA) and the polydiacetylenes (PDAs) is a well understood electron correlation effect. Excited states in these centrosymmetric systems have A_g or B_u symmetry, which can be further classified according to their charge-conjugation symmetry¹. The dipole selection rule allows optical transitions only between A_g and B_u states of opposite charge-conjugation symmetries, and the optical transition from the $1A_g$ ground state to the $1B_u$ state with opposite charge-conjugation symmetry is strongly allowed. Due to the moderate strength of the on-site electron-electron (e-e) interaction (the Hubbard U) in these systems, however, the lowest dipole-forbidden $2A_g$ state occurs below¹⁻⁴ the $1B_u$, and the optically pumped $1B_u$ decays in ultrafast times to the $2A_g$, radiative transition from which to the $1A_g$ is forbidden.

Strong PL from π -conjugated polymers like poly(para-phenylene) (PPP), poly(para-phenylenevinylene) (PPV) and their derivatives is also by now well understood. As shown by Soos and collaborators^{5,6} the lowest excited states of these systems can be understood within *effective* linear chain models with large bond alternation. Schematically, materials like PPP and PPV can be thought of as obtained by replacement of all or alternate double bonds in t-PA with benzene moieties, a process we term as “bond substitution”, that in effect increases the bond alternation of the effective linear chain⁷. The enhanced bond alternation leads to a reversed energy ordering $E(2A_g) > E(1B_u)$ (where $E(\dots)$ is the energy of the state in question), which is conducive to strong light emission.

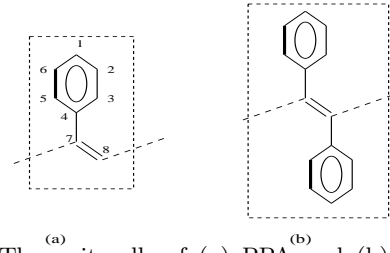


FIG. 1. The unit cells of (a) PPA and (b) PDPA. The phenyl rings are rotated with respect to the y -axis, which is transverse to the axis of the polyene backbone (x -axis)

The recent observation of strong PL in phenyl-disubstituted polyacetylenes (PDPAs) (see Fig. 1)⁸⁻¹³ is difficult to explain within the above simple theoretical picture. These systems consist of a backbone polyene chain, the hydrogen atoms of which have been replaced with phenyl groups¹⁴, a process that we term as “site substitution”, in order to distinguish it from bond substitution. Since the Hubbard U for the backbone polyene carbon atoms (the repulsion between two π -electrons occupying the same backbone atom), is an atomic property, it should have the same magnitude in the PDPAs and polyenes. Since the one-electron hopping integrals between the backbone atoms are also expected to have similar magnitudes, the observed PL is perplexing. Several different explanations of this apparently peculiar behavior are possible, and one goal of the present paper is to arrive at the correct mechanism of the PL. A brief presentation of our work has been reported earlier¹⁵. Here we present more detailed work with a broader goal, viz., to understand the $2A_g - 1B_u$ crossover that we show occurs in these systems from a global perspective for the family of π -conjugated polymers. Specifically, we are in-

terested in the *mechanism* of the crossover, and not just the result. We show that there are two different manifestations of the so-called “electron correlation effect”, and as far as the relative location of the $2A_g$ is concerned, the two effects are competing. The effect of the spin-dependent Hubbard correlation is to always lower the energy of the $2A_g$ and to increase the energy of the $1B_u$. A second correlation effect can be the confinement of electrons and holes in the excited $1B_u$ state, which has been discussed only in the context of excitons^{16,17}. Although the Hubbard U causes ground state localization, it has a weak effect on the electron-hole confinement in the excited state, and the origin of any such confinement therefore has to be different. There can be multiple origins of this confinement, but in perhaps all these cases the consequence is either the lowering of $E(1B_u)$, or the raising of $E(2A_g)$, or both, i.e., the opposite of the effect due to the Hubbard U . Our aim in the present paper is to give a clear understanding of how this confinement occurs in the PDPAs.

A second goal of the present work is to understand and predict the optical absorption in phenyl-substituted acetylenes over a wide wavelength region. In the past, theoretical and experimental work on the polarizations of the high energy absorptions in oriented samples of PPV have considerably increased our understanding of electron correlation effects in this system^{18–21}, and it is our hope that similar polarized absorption measurements will be carried out on oriented samples of phenyl acetylenes as they become available.

In order to discuss the applications of our results to real materials, we need to clarify several aspects of the experiments with the phenyl-substituted polyacetylenes. Before proceeding further, we therefore present a brief overview of the experimental situation^{8,9,12,13}. Three different classes of phenyl acetylenes have been synthesized, which include, (i) poly-phenylacetylenes (PPAs), which are obtained by substituting alternate hydrogen atoms of t-PA with phenyl groups¹⁴, (ii) poly-phenylalkylpolyacetylenes (PAPAs), in which alternate hydrogens of t-PA are replaced with alkyl and phenyl groups¹⁴, respectively, and (iii) the PDPAs, already mentioned above. In Figs. 1(a) and (b) we have shown the structures of PPA and PDPA, respectively. The PPAs are weak emitters, while whether or not the PAPAs emit light depends on the size of the alkyl group, – for small alkyl groups the PL quantum efficiency is small while for large alkyl groups this can be as large as in PDPAs (see Fig. 6 in reference 9). In contrast, all PDPAs are strong emitters of light, in the green or blue region of the spectrum. Raman scattering studies that have probed the backbone $C = C$ bonds have determined that the conjugation lengths of PAPAs and PDPAs are short¹⁰ (5 – 7 double bonds along the backbone according to the authors). The finite conjugation length is perhaps to be anticipated, based on the large sidegroups that are apt to lead to twists and bends involving the backbone main chain. Finally, in both PPAs and PDPAs (see Fig. 1)

steric effects involving the phenyl groups would be considerable, and moderate phenyl group rotations are to be expected. There is currently no experimental information on the extent of this ring torsion.

In principle, there can be multiple reasons for the observed light emission in PDPAs. First, the light emission can be a simple consequence of the loss of C_{2h} symmetry due to ring torsions. Within this scenario the nominally $2A_g$ occurs below the $1B_u$, but in the absence of strict symmetry classification, this state is emissive¹⁰. Second, the energy ordering *is* reversed, i.e., $E(2A_g) > E(1B_u)$, but this is a simple consequence of finite conjugation lengths, – it is, for example, believed that in the shortest polyenes the $2A_g$ might occur above the $1B_u$. Third, it is conceivable that the light emission is a consequence of an intricate electronic mechanism that involves the electron hopping among the phenyl groups. Referring to Fig. 1, for example, even with ring torsions the distances between consecutive phenyl groups on the same side of the backbone polyene chain in both PPA and PDPA are rather small. If these are now nearly coplanar (i.e., if the ring torsions are ordered) there should be considerable overlaps between the π -electron clouds of the phenyl groups, leading to electron hoppings between them²², as is well-known in the literature on segregated stack organic charge-transfer solids²³. Fourth, it is conceivable that phenyl-substitution leads to enhanced bond alternation on the backbone polyene chain, and this is what leads to the reversed energy ordering and light emission, exactly as in PPV and PPP²⁴. Finally, light emission can be a consequence of confinement or localization along the backbone, which is accompanied by enhanced delocalization into the phenyl sidegroups¹⁵. We have ignored in the above the possibility that excited state ordering $E(2A_g) > E(1B_u)$ is due to the relaxation of the $1B_u$ exciton, as the $1B_u - 2A_g$ energy gap in t-PA is known to be fairly large, and even if exciton relaxation plays a role, this would still require that this energy gap in PDPAs has shrunk due to an electronic mechanism.

We point out that the experimental results already preclude most of the possible scenarios. The loss of C_{2h} symmetry is stronger in PPAs than in PDPAs, and if the light emission was from the nominally $2A_g$ state, one would have expected these to be more strongly emissive than the PDPAs. Furthermore, in our explicit calculations for PPA, we have found that the transition dipole coupling between the nominally $2A_g$ and the nominally $1A_g$ *is* nonzero, but its magnitude remains very small (we therefore continue to refer to eigenstates as A_g and B_u , even though this classification is not strictly valid). Lack of C_{2h} symmetry is therefore not the origin of the strong PL. Finite conjugation length alone cannot explain the light emission, as the estimated conjugation lengths¹⁰ are in the region where the $2A_g$ occurs below the $1B_u$ in the polyenes²⁵. The direct electron hopping between the phenyl groups do introduce a novel conjugation channel absent in other π -conjugated polymers, but this effect should be comparable in the PPAs, PAPAs and PDPAs.

The absence of strong PL in the PPAs and many PAPAs then again precludes this mechanism. Indeed, as we show from explicit calculations, this particular interaction affects the lowest energy allowed and forbidden optical gaps very weakly, although it can have a strong effect on the optical absorption in the high energy region. Thus from the experiments alone, we believe that there are only two possible explanations of the strong PL in PDPAs, viz., enhanced bond alternation and an electron correlation induced confinement-delocalization effect. Our previous work had already shown that the bond alternation is smaller in the PDPAs than in t-PA. In the present work we show further detailed work, emphasizing on the mechanism behind the reduced bond alternation, rather than the result itself. Our aim is to show that this effect and the confinement effect are ultimately related, and even though the $2A_g - 1B_u$ crossover is a many-body problem, the final results could have been perhaps anticipated from a combination of our understanding of one-electron theory and confinement effects due to e-e interactions.

In the rest of the paper we present detailed calculations for PPA and PDPA oligomers and polymers. We do not present explicit calculations for PAPA, the understanding being that the effect of the alkyl groups on the electronic structure is by and large the same as that of the hydrogen atoms, with the only difference that the site energies (electronegativities) of the backbone carbon atoms to which the alkyl groups are bonded might be weakly different. We postpone comments on the strong PL from PAPAs with very large alkyl groups until the last section of the paper. In section II we present our Hamiltonian, along with a detailed discussion of the parameters. In section III we give a brief discussion of known results concerning the effect of confinement on the $2A_g - 1B_u$ crossover in linear chains. These discussions point out already the necessity to have a precise understanding of the electronic structures of PPA and PDPA within the one-electron limit of our Hamiltonian, our results for which are presented in section IV. In section V, we present details of the optical absorption within the correlated Hamiltonian within the singles-configuration interaction (SCI) approach. The goal of this section is two-fold. First, we show that the electron-hole confinement along the backbone has a synergistic relationship with the delocalization into the phenyl rings. A second goal is to make specific predictions that can be tested out in absorption studies of oriented samples in the future. In section VI, we present the results of multiple reference singles and doubles configuration interaction (MRSDCI) studies⁴ on short PPA and PDPA oligomers to prove the reversed energy ordering in these systems. These calculations are considerably more sophisticated than our previously reported calculations¹⁵, but nevertheless, slightly longer oligomers could be investigated here. In section VII we present our concluding discussions, emphasizing the fact that the mechanism of $2A_g - 1B_u$ crossover found here introduces the novel possibility of synthesizing light emitting π -conjugated polymers

with small optical gaps¹⁵.

II. THEORETICAL MODEL

Our calculations are within the π -electron model for PPAs and PDPAs, as the ordering of the lowest energy states depends primarily on the electron correlation effects among the π -electrons. Even with this restriction, the complete theoretical model for PPAs and PDPAs is rather complicated, as this must include the effects of the electron-phonon (e-ph) couplings along the backbone polyene chain, electron-electron (e-e) interactions among all the π -electrons, and all effects of phenyl-group rotations. Phenyl-group rotations modify the one-electron hoppings between the phenyl groups and the backbone chain and the intersite Coulomb interactions involving the carbon atoms of the phenyl groups, and in addition, introduce σ -type bondings between the π -molecular orbitals (MOs) of neighboring phenyl groups on the same side of the polyene chain. This last interaction is maximized when the rotational angle is ordered and 90° , but such large rotation would completely destroy the phenyl-polyene conjugation, leading to an effectively isolated polyene chain and isolated benzene molecules. Since the properties of PPAs and PDPAs are different from those of isolated polyene chains, the rotation angle must be considerably less than 90° , in which case the one-electron hoppings between neighboring phenyl groups can involve only a few of the carbon atoms of each phenyl group (see Fig. 1).

From the above, the overall Hamiltonian for PPAs and PDPAs is written as,

$$H = H_C + H_B + H_{CB} + H_{BB} + H_{ee}, \quad (1a)$$

Here H_C and H_B are the one-electron Hamiltonians for the backbone chain carbons and the benzene units, respectively, H_{CB} and H_{BB} are the one-electron hoppings between the chain and the phenyl units, and between the phenyl groups themselves, respectively, and H_{ee} is the e-e interaction. The individual terms can now be written as,

$$H_C = - \sum_{\langle k, k' \rangle, M} (t_0 - \alpha \Delta_{k, M}) B_{k, k'; M, M+1} + \frac{1}{2} K \sum_{k, M} \Delta_{k, M}^2 \quad (1b)$$

$$H_B = -t_0 \sum_{\langle \mu, \nu \rangle, M} B_{\mu, \nu; M, M} \quad (1c)$$

$$H_{CB} = -t_\perp \sum_{\langle k, \mu \rangle, M} B_{k, \mu; M, M}, \quad (1d)$$

$$H_{BB} = - \sum'_{\mu, \nu, M, M'} t_\sigma(\mu, \nu) B_{\mu, \nu; M, M'} \quad (1e)$$

$$H_{ee} = U \sum_{i,M} n_{i,M,\uparrow} n_{i,M,\downarrow} + \frac{1}{2} \sum_{i \neq j, M, N} V_{i,j,M,N} (n_{i,M} - 1)(n_{j,N} - 1) \quad (1f)$$

In the above, k, k' are carbon atoms on the polyene backbone, μ, ν are carbon atoms belonging to the phenyl groups, M is a composite site consisting of a phenyl group and a polyene carbon, $\langle \dots \rangle$ implies nearest neighbors, and $B_{i,j,M,M'} = \sum_{\sigma} (c_{i,M,\sigma}^{\dagger} c_{j,M',\sigma} + h.c.)$. The t_0, t_{\perp} and $t_{\sigma}(\mu, \nu)$ are matrix elements corresponding to one-electron hops, where t_{σ} depends on the particular μ, ν being considered. In H_C , α is the e-ph coupling constant, K the spring constant, and $\Delta_{k,M} = (u_{k+1,M+1} - u_{k,M})$, where $u_{k,M}$ is the displacement of the M th composite site from equilibrium. In H_{CB} , the sum over μ is restricted to atoms of the phenyl groups that are directly bonded to backbone carbon atoms. The prime on the summation in H_{BB} indicates that the sum is restricted to a few carbon atoms of neighboring phenyl groups that are on the same side of the polyene chain (*i.e.*, $M' = M \pm 2$), the actual number depending upon the extent of phenyl group rotation. H_{ee} is the e-e interaction, with i and M including now all atoms. The Coulomb interactions are parametrized according to the Ohno relationship²⁶,

$$V_{i,j,M,N} = U / (1 + 0.6117 R_{i,j,M,N}^2)^{1/2}, \quad (2)$$

where $U = 11.13$ eV and $R_{i,j,M,N}$ is the distance in Å between the i th carbon in unit M and the j th carbon in unit N . The Ohno parametrization is for small molecules, and it is conceivable that the Coulomb parameters for the polymeric samples are somewhat smaller²⁷. Our aim, however, is to obtain a *qualitative* understanding of the role played by e-e interactions on the optical properties of the system. We have therefore employed large H_{ee} to show that in spite of these large interactions energy ordering $E(2A_g) > E(1B_u)$ will occur in the substituted polyacetylenes. The same considerations apply to the other parameters (see below), *viz.*, the actual numerical values are relatively unimportant, as our goal is to extract the essential physics of these systems.

In our calculations the backbone polyene atoms were assumed to lie in the xy plane, with the x direction defined as the polymer axis (see Fig. 1). Due to steric effects, the phenyl rings will not be in the xy plane, but will be rotated with respect to the y axis. All intra-phenyl bond lengths are taken to be 1.4 Å and the bond between the backbone atoms and the phenyl groups is taken to be a true single bond with length 1.54 Å. In our calculations of bond-alternation along the polyene backbone (section IV), the backbone polyene bond lengths are assumed to be 1.4 Å in the undistorted configuration, while the bond lengths are calculated self-consistently in the distorted configuration. The calculations of optical absorption are for finite oligomers, in which we chose the backbone bond lengths the same as in t-PA, *viz.*, 1.45 Å

and 1.35 Å, for reasons to be discussed later. We considered both parallel and antiparallel ordered rotations of the phenyl groups bonded to the nearest neighbor carbon atoms in PDPA (note that these occur on opposite sides of the backbone, the phenyl groups on the carbon atoms on the same side of the chain are parallel in both cases) with rotation angles of 30° (this value of the torsional angle is of course arbitrary; on the other hand torsional angles larger than 45° will decrease t_{\perp} drastically). However, the differences in numerical results (energies as well as transition dipole couplings) for the two cases were insignificant. Therefore, we restricted our studies to the parallel configuration for the phenyl groups, rendering the symmetry group of PDPA to be C_i , with identity and inversion operators as symmetry elements. PPA, on the other hand, does not possess any point group symmetry.

As far as the hopping matrix elements are concerned, we assumed $t_0 = 2.4$ eV. Along the backbone carbon atoms, whenever rigid bond alternation was assumed along the chain, standard values of 2.2 eV and 2.6 eV were chosen for the long and the short bonds, respectively. The aforesaid rotation of the phenyl groups with respect to the y axis will have the effect of reducing the hopping integral t_{\perp} connecting the phenyl rings to the t-PA backbone, as compared to the standard value of 2.4 eV. Various possible values for t_{\perp} were considered in our calculations. We postpone the discussion of our choice of $t_{\sigma}(\mu, \nu)$ until later.

III. CONFINEMENT AND THE $2A_g$ - $1B_u$ CROSSOVER

Although the theory of $2A_g - 1B_u$ crossover is well understood in linear chains, it is useful to present a brief review in view of what follows. Consider the rigid bond limit of Eq. (1) for the case of linear chains, with $t_{\perp} = 0$ and the chain hopping integrals $t_0(1 \pm \delta)$. In the limit of large U , the ground state has all atoms singly occupied by electrons and the $2A_g$ is a spin excitation that is sum of two triplets, each localized on the double bonds, and has the energy $4t^2(1 + \delta)^2 / (U - V)$, where V is the Coulomb interaction between nearest neighbor atoms on the linear chain¹⁻⁴.

For finite U , the overall wavefunction is a superposition of this spin excitation and a charge excitation, and the $2A_g$ occurs below the $1B_u$ if the contribution of the spin excitation configuration dominates over that of the charge excitation configuration. From configuration interaction principles, the relative contribution of the spin excitation decreases as its energy increases, and therefore both increasing δ (for fixed U and V) and increasing V (for fixed U and δ) will increase the energy of the $2A_g$ relative to the $1B_u$. This can be understood physically in the limit of large δ or V rather easily. The spin excitation that is relevant in the description of the $2A_g$ is obtained

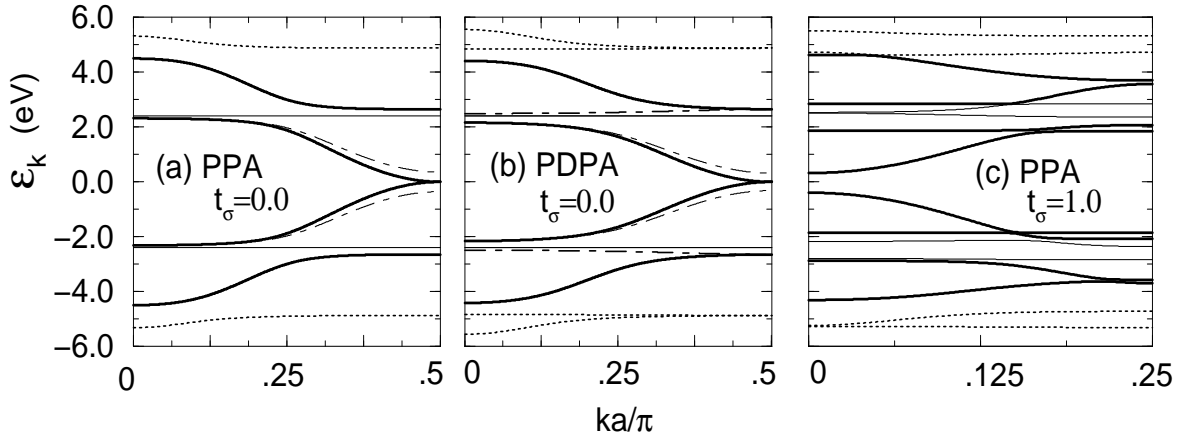


FIG. 2. Band structures of (a) PPA and (b) PDPA for $t_{\perp}=1.4$ eV and $t_{\sigma} = 0$, and (c) PPA for $t_{\perp}=1.4$ eV and $t_{\sigma} = 1.0$ eV. Here thick solid lines represent polyene chain-derived bands, with zero bond alternation in (a) and (b), and with finite bond alternation in (c). Finite bond alternation in (a) and (b) opens a gap at the Fermi level, and the highest valence and lowest conduction bands in these cases are shown as thin dashed-dotted lines. The thin solid lines represent benzene-derived localized bands (see text) and the thick dashed-dotted lines in (b) represent benzene-derived delocalized bands. There occur delocalized benzene-derived bands in (a) which are nearly degenerate with the flat localized bands and are not visible within our resolution.

from the localized ground state by two consecutive electron hops in opposite directions, the first creating a virtual state with a doubly occupied site and a vacancy, and the second destroying this. Now increasing δ or V both have the tendency to confine the double occupancy and the vacancy in the virtual state to nearest neighbor dimer ethylenic units, and since the dimer does not have a spin singlet covalent excitation, there always exist a δ or V where $E(2A_g) > E(1B_u)$, with the only condition that δ is nonzero to begin with. Thus any interaction that confines the double occupancy and the vacancy in the virtual state should increase the *relative* energy of the $2A_g$. We refer to references 5,6 for further details on the effect of δ , but point out a fundamental difference between the effect of δ and V on the $1B_u$. While increasing δ (for fixed U and V) increases $E(1B_u)$, increasing V (for fixed U and δ) decreases $E(1B_u)$ (since the correlation contribution to the optical gap is linear in $U - V$). Although increasing V is not a practical proposition in linear chains, the more important point is that in principle at least, energy ordering conducive to light emission does not necessarily require that $E(1B_u)$ be larger than in the polyenes or t-PA.

Recognition that any interaction that promotes confinement of the vacancy and the double occupancy in the virtual state allows us to understand the *mechanism* of a possible $2A_g - 1B_u$ crossover in PDPA by probing the $1B_u$ in detail, since the same interaction will also lead to confinement in the $1B_u$. Now, probing the $1B_u$ theoretically is much simpler than probing the $2A_g$. This is because the SCI approximation, which is easy to implement, is known to give a reasonable description of the $1B_u$, but not that of the $2A_g$. Any possible confinement in the $1B_u$ in PPA and PDPA can only occur due to conjugation with the phenyl sidegroups, and in order to understand the effects of this conjugation in detail we

have to start from one-electron theory, as is done in the next section.

IV. ONE-ELECTRON THEORY

In this section we present the results of our calculations of band structures, bond alternations, and optical absorptions in PPA and PDPA based upon one-electron theory ($H_{ee} = 0$ within Eq. (1)). It will be seen that the difference between PPA and PDPA on the one hand, and polyenes on the other, can be largely understood already within one-electron theory, and the effects of e-e interactions can be anticipated based upon these results.

A. Band Structure

The band structures were calculated within the rigid bond approximation, and two different cases, viz., equal bond lengths and bond lengths corresponding to those of t-PA along the polyene backbone were considered. Furthermore, since the number of carbon atoms to be retained in H_{BB} is somewhat arbitrary (as the exact extent of the overlap between the π -MOs of neighboring phenyl groups is difficult to estimate) we perform two different sets of band structure calculations, with H_{BB} both zero and nonzero. As these calculations indicate, the strongest effects of phenyl substitution in the region close to the Fermi level are those due to H_{CB} , with H_{BB} playing a smaller quantitative role. H_{BB} , however, plays a stronger role away from the Fermi level.

For $H_{BB} = 0$ the one-electron part of Hamiltonian (1) is the simple Hückel model. In this case, the consequence of nonzero H_{CB} is simple hybridization between the polyene bands and benzene molecular orbitals

(MOs). The highest (lowest) occupied (unoccupied) benzene MOs (HOMOs and LUMOs) are doubly degenerate, with one member of each set of doubly degenerate levels being delocalized over all the carbon atoms of the benzene molecule and the other localized over four of the six carbons²⁸. Henceforth, we refer to the delocalized HOMO (LUMO) as d (d^*) and the localized HOMO (LUMO) as l (l^*). We expect very strong hybridization between the polyene valence (conduction) bands and the d (d^*) MOs, but the l and l^* MOs are expected to retain their characters, as in the case of PPV^{18,19,27,29}. In addition to the d , d^* frontier MOs, each benzene molecule also has a delocalized low (high) energy occupied (unoccupied) MO, hybridization between which and the polyene-derived bands is expected to be smaller (except at the edge of the Brillouin zone) due to the large one-electron energy difference.

In Figs. 2 (a) and (b) we have shown the band structures for PPA and PDPA, respectively, for $H_{BB} = 0$, but nonzero H_{CB} , with $t_{\perp} = 1.4$ eV. We have verified that the band structure remains qualitatively the same for all t_{\perp} between 1 eV and 2.0 eV. For the case of zero bond alternation, there exists a Fermi surface degeneracy, exactly as in the case of t-PA, indicating unconditional bond alternation in the infinite chain limit. The band structures are nearly identical for zero and nonzero bond alternation, except at the center of the Brillouin zone, where a gap opens up for nonzero bond alternation in both PPA and PDPA.

For phenyl group rotations of 30° - 45° , H_{BB} has significant contributions only from the overlaps between the carbon atoms 2 and 6', and between atoms 3 and 5' in Fig. 1 (here 6' and 5' refer to carbon atoms equivalent to 6 and 5, on the next phenyl group on the same side of the polyene chain). We will therefore ignore the more distant $t_{\sigma}(\mu, \nu)$ and will henceforth refer to the nearest neighbor terms that we retain as simply t_{σ} . In the absence of theoretical and experimental information concerning the magnitudes of these hopping integrals, we have chosen relatively large values of 1.0 eV and 2.0 eV, to determine the largest effects of H_{BB} . The band structure of PPA for the case of $t_{\sigma} = 1.0$ eV is shown in Fig. 2(c). There are two effects of nonzero H_{BB} . First, charge conjugation symmetry is broken. Second, there is now much larger dispersion in the "benzene-derived" bands. However, the gap between the highest valence band and the lowest conduction band remains largely unaffected, a result that remains true even for $t_{\sigma} = 2.0$ eV (not shown). Due to the doubling of the unit cell upon inclusion of H_{BB} the Brillouin zone is halved and the number of bands for PPA is twice those in Fig. 2(a). In the case of PDPA this number is larger by almost another factor of two, and we have therefore not shown the band structure for PDPA for nonzero t_{σ} . As in PPA, however, H_{BB} has an insignificant effect on the energy gaps in the low energy region. We therefore do not expect the low energy physics (especially the energy ordering upon inclusion of H_{ee}) to be altered by H_{BB} . On the other hand, because

of the larger dispersion in the benzene-derived bands, nonzero H_{BB} leads to chain-to-benzene charge-transfer absorptions at relatively lower energy (see below).

From the band structures alone, the strong hybridization that occurs between the polyene bands and the benzene delocalized HOMO and LUMO are obvious only away from the center of the reduced Brillouin zone ($k = \pi/2a$ in Figs. 2(a) and (b) and $k = 0$ in Fig. 2(c)). A more quantitative measure of the hybridization, however, is the contribution of the chain atoms to the band wavefunctions. We have calculated this quantity for the one-electron wavefunction corresponding to the Fermi level k_F , defined as, $\rho_{c,k_F} = \sum_{i \in chain} c_{k_F,i}^* c_{k_F,i}$, where $c_{k_F,i}$ is the coefficient of the i th chain atom to the wavefunction at $k = k_F$, for both PPA and PDPA as a function of t_{\perp} . In Fig. 3(a) we have summarized our results, where we see that ρ_{c,k_F} decreases rapidly with t_{\perp} . Similar calculations were done also for one-electron levels away from k_F . In general, the chain contribution to the highest occupied and lowest unoccupied bands decreases with increasing absolute value of the one-electron energy (there of course exists a sum rule, which implies that the nominally benzene-derived bands away from the Fermi level have considerable contribution from the polyene chain atoms). Since the Peierls bond-alternation in t-PA is a strictly one-dimensional effect, the large decrease in ρ_{c,k_F} with t_{\perp} indicates that the bond-alternation in PPA and PDPA should be smaller than in t-PA.

B. Bond Alternation

For bond alternation within a periodic configuration, $u_{k,M} = (-1)^M u_0$ in Eq. (1). We have calculated the optimal bond alternation u_0 , within the one-electron limit ($H_{ee} = 0$) of Eq. (1). The magnitude of u_0 depends on the dimensionless e-ph coupling constant α^2/Kt_0 , but the qualitative behavior as a function of t_{\perp} does not. We have therefore chosen the original Su-Schrieffer-Heeger³⁰ values of α (4.1 eV/Å) and K (21 eV/Å²), for direct comparisons to previous one-electron theories of t-PA. In reference 15, we had shown the behavior of finite PDPA rings with variable size for a few fixed t_{\perp} . Here we show the behavior of both PPA and PDPA for $0 < t_{\perp} < 2.0$ eV in Fig. 3(b). These results are for periodic rings containing 100 backbone carbon atoms, where the optimal u_0 has reached its saturation value in all cases. The close relationship between the optimal u_0 and ρ_{c,k_F} is obvious from the natures of these curves.

As has been argued in reference 15, nonzero H_{ee} will change the magnitude of u_0 in each polymer, but will not change the trend seen in Fig. 3 (b), viz., a reduction in the bond alternation with increasing t_{\perp} . We therefore conclude that the observed PL in PPA and PDPA cannot be a consequence of large effective bond alternation, as is true in the bond-substituted materials PPP and PPVs.

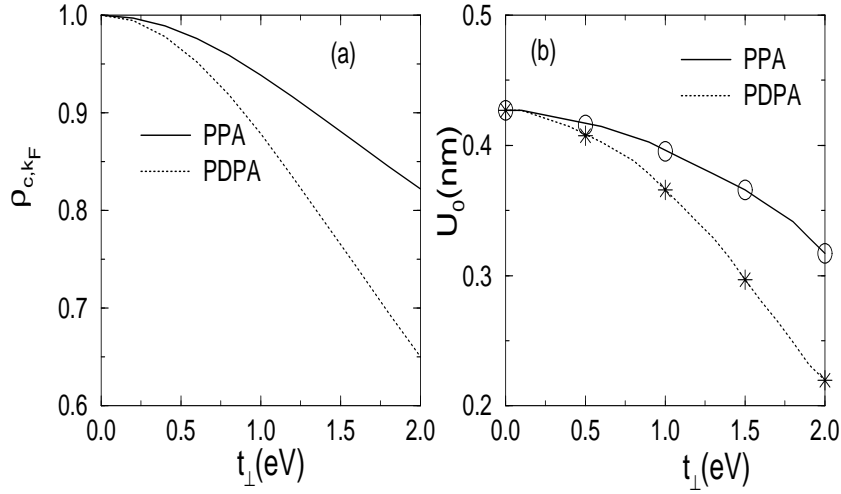


FIG. 3. (a) The contributions by the polyene chain atoms to the one-electron wavefunction at $k = k_F$ in PPA and PDPA, as a function of t_\perp for $t_\sigma = 0$. Nonzero t_σ has almost no effect on ρ_{c,k_F} . (b) The self-consistent bond alternation (in nanometers) within the one-electron limit of Eq. (1), as a function of t_\perp . The continuous curves are for $t_\sigma = 0$, while the stars (\star) and circles (\circ) correspond to $t_\sigma = 1.0$ eV for PDPA and PPA, respectively, again indicating the insignificant effect of t_σ on the low energy properties.

C. Optical absorption

Although our interest lies primarily in calculating the optical absorption with nonzero H_{ee} , it is useful to discuss the $H_{ee} = 0$ limit first. In the case of PPV, comparisons of absorption spectra calculated within one-electron and many-electron theories on the one hand, and with experimental spectra on the other^{19,20}, have led to a clear understanding of the effects of the e-e interaction. Although oriented samples of phenyl-substituted polyacetylenes do not exist at the moment, we give details of the calculated polarizations here, in anticipation of future experimental work.

The optical absorption within one-electron theory can be anticipated from the structures of PPA and PDPA. In the absence of H_{CB} and H_{BB} we expect isolated low energy polyene chain absorption polarized primarily along the x -axis, and degenerate benzene transitions at high energy which can be characterized as $d \rightarrow d^*$ (y -polarized), $l \rightarrow l^*$ (y -polarized) and $d \rightarrow l^*$ and $l \rightarrow d^*$ (x -polarized) (these polarizations can be anticipated from previous work on PPV, as the unit cell in PDPA is simply the trans-stilbene molecule). The anticipated effects of nonzero H_{CB} are: (i) enhanced y -character in the lowest energy chain absorption due to hybridization with the benzene delocalized MOs, (ii) splitting of the high energy molecular benzene transitions, and (iii) new degenerate chain \rightarrow benzene and benzene \rightarrow chain charge-transfer type absorptions at intermediate energies. The charge-transfer type absorptions will include transitions from and to benzene d , d^* and l , l^* orbitals. Of these, the former (involving d , d^* MOs) are expected to have mixed polarization (since these are hybridized with the chain-derived bands that have some y -character, see above), but the latter (involving l , l^* MOs) should be primarily x -polarized. From the band structures in Figs. 2(c),

for nonzero H_{BB} we expect even larger splitting in the molecular transitions, and thus the width of the absorption band in this region should increase. Due to broken charge-conjugation symmetry, the chain \rightarrow benzene and benzene \rightarrow chain absorptions are also nondegenerate, and therefore the absorption band in the intermediate energy should also be broader.

In Figs. 4 (a) and (b) we have shown the absorption spectra of finite PPA and PDPA oligomers with eight double bonds along the polyene chain for nonzero H_{CB} ($t_\perp = 1.4$ eV) but $H_{BB} = 0$. Our choice of finite oligomers is based on the finite conjugation lengths of the existing materials¹⁰. The hopping integrals along the polyene backbone here are 2.2 eV and 2.6 eV, corresponding to those of t-PA. This is primarily because it is difficult to estimate the extent of the bond alternations in finite chains, but also because the polarizations and the oscillator strengths of the various transitions depend weakly on the magnitudes of the hopping integrals, and even the energies of the higher energy transitions do not depend on these, as we have verified from explicit calculations. We have indicated in Fig. 4 the polarizations of the different absorption bands. The oscillator strength of the lowest energy chain \rightarrow chain absorption is the same in both cases, but that of the high energy molecular absorption (centered around $2t_0 = 4.8$ eV) in PDPA is nearly twice that in PPA. The large width of this absorption is due to the nondegeneracy of the molecular transitions. At intermediate energy, the weak second and third peaks correspond to chain HOMO - 1 \rightarrow LUMO + 1 and HOMO - 2 \rightarrow LUMO + 2 transitions, following which there occur the charge-transfer transitions. The absorption spectra for other t_\perp can be guessed from Fig.

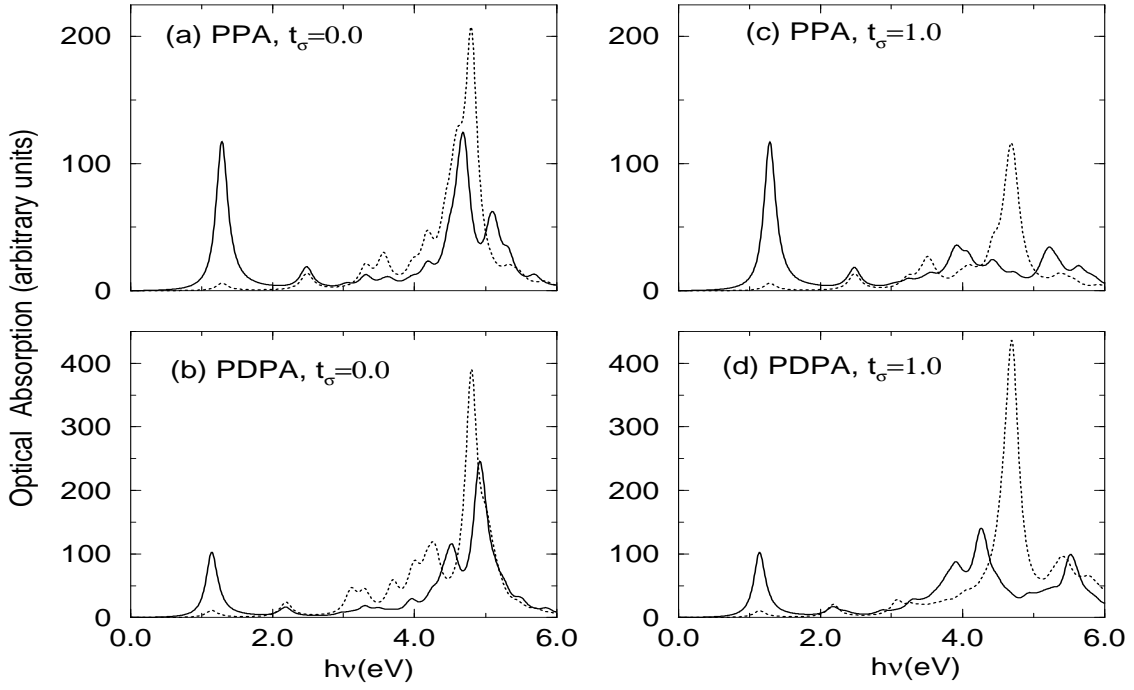


FIG. 4. The calculated x (solid line) and y (dotted lines) components of the optical absorption spectra within one-electron theory for finite PPA (Figs. (a) and (c)) and PDPA (Figs. (b) and (d)) oligomers with eight double bonds on the backbone polyene chain. The y-axis scales are different for PPA and PDPA. In all cases $t_{\perp} = 1.4$ eV, while $t_{\sigma} = 0$ in Figs. (a) and (b) and 1.0 eV in Figs. (c) and (d)).

4(a) and (b). Specifically, larger (smaller) the t_{\perp} , the broader (narrower) is the molecular absorption and the stronger (weaker) are the charge-transfer type absorptions.

The absorption spectra for the case of nonzero H_{BB} are shown in Figs. 4(c) and (d). With increasing t_{σ} , the molecular absorptions are broader, the charge-transfer transitions are redshifted and acquire greater width.

V. OPTICAL ABSORPTION FOR NONZERO H_{ee}

There are two goals of our work in this section. First, we demonstrate that the polarization characters of the lowest absorption in PPA and PDPA change radically for nonzero H_{ee} , and that this change in the polarization character provides the hint to understanding the mechanism of the $2A_g - 1B_u$ crossover that occurs in PDPA. Second, a strong x -polarized charge-transfer type absorption appears at intermediate energy when both H_{ee} and t_{σ} are nonzero. This intermediate energy absorption may have already been seen experimentally in unoriented samples (see Fig. 2 in reference 9). In the following we discuss the energies and the polarizations of the lowest energy absorption and the overall absorption spectra separately.

A. Lowest energy absorption.

Our calculations of the optical transitions are within the SCI approximation. The SCI is known to give rea-

sonable descriptions of the odd parity B_u states (especially the lowest B_u state, the $1B_u$), even though it is a poor approximation for the even parity A_g states. In Table I we have given the optical gaps of PPA and PDPA oligomers with eight double bonds for $H_{CB} \neq 0$, but $H_{BB} = 0$ (reference 15 discusses the case of five double bonds). These calculations are within the rigid bond approximation, with the hopping integrals along the chain 2.2 eV and 2.6 eV, for single and double bonds, respectively. We show later that as within one-electron theory, the role played by H_{BB} in the low energy region is weak.

TABLE I. Optical gaps of oligomers of PDPA and PPA, containing eight double bonds in the backbone chain, within the Hückel and the Coulomb correlated models, as a function of t_{\perp} . Calculations based upon the correlated model were performed within the SCI approximation. Note that the case of $t_{\perp} = 0.0$ corresponds to the eight double-bond polyene. All energies are in the units of eV.

t_{\perp}	PPA		PDPA	
	Hückel	SCI	Hückel	SCI
0.00	1.45	3.26	1.45	3.26
0.35	1.44	3.17	1.42	3.08
0.70	1.40	3.13	1.35	3.01
1.40	1.28	3.02	1.14	2.80
1.80	1.20	2.94	1.01	2.65

As seen in Table I, the optical gap decreases with t_{\perp} . Interestingly, the decrease (relative to $t_{\perp} = 0$) is greater for nonzero H_{ee} than for $H_{ee} = 0$, a result that is a consequence of increased delocalization of the excited electron and hole of the $1B_u$ into the phenyl components for nonzero H_{ee} , as we show below. The existing PPA and PDPA materials are finite oligomers¹⁰, but for true long chain materials correct calculations of the optical absorption should include self-consistent calculations of the bond alternation (instead of the rigid bond approximation adopted here). In such a case, even larger decrease in the optical gap would be obtained. In the existing literature it is often assumed that PPA and PDPA have larger optical gaps than t-PA, but this is a consequence of the finite sizes of the substituted materials. The optical gaps of the substituted materials are smaller than the polyenes with the same chain length, with the gap in PDPA smaller than that in PPA.

In Table II we have given the x - and y -components of the transition dipole couplings μ_x and μ_y between the ground state and the $1B_u$ state of the PDPA oligomer (the electronic charge is taken as 1, and the dipole couplings are in units of Å). The transition dipole coupling is known to be a direct measure of the electron-hole correlation length in the $1B_u$. We do not show similar results for PPA, as the difference is only quantitative. There are three interesting features of these results. First, for each t_{\perp} , μ_x decreases for nonzero H_{ee} , a result that is common to all other π -conjugated polymers, and is a signature of exciton formation and confinement of the electron-hole pair^{16,17} in the $1B_u$ in the x -direction for nonzero H_{ee} . Second, t_{\perp} decreases μ_x for both $H_{ee} = 0$ and $\neq 0$, but this decrease is considerably larger for nonzero H_{ee} . For example, the decrease in μ_x between $t_{\perp} = 0$ and $t_{\perp} = 1.8$ eV is 2.6 % for $H_{ee} = 0$ but 8.2 % for $H_{ee} \neq 0$. This effect is reminiscent of the effect of t_{\perp} on the optical gap (see above), and is a signature of greater longitudinal electron-hole confinement for nonzero t_{\perp} when H_{ee} is nonzero. Note that with the Ohno Coulomb parameters, which are intermediate in strength, relatively small increase in the confinement can lead to $2A_g - 1B_u$ crossover. In the case of linear chain polyenes within the rigid bond approximation (*i.e.*, hopping integrals $t_0(1 \pm \delta)$) the difference in the electron-hole correlation length in the $1B_u$ state³¹ between $\delta = 0.07$ ($E(2A_g) < E(1B_u)$) and $\delta = 0.3$ ($E(2A_g) > E(1B_u)$) is only 7 %. In the present case, the increased longitudinal confinement is accompanied, as well as driven, by the electron correlation induced delocalization in the transverse direction, as observed from the very interesting behavior of μ_y . As seen in Table II nonzero H_{ee} increases μ_y for arbitrary fixed t_{\perp} , which is completely contradictory to the behavior in the x -direction. To the best of our knowledge, increasing transition dipole coupling with H_{ee} has not been found in any other π -conjugated system. As noted in reference 15 the μ_y corresponding to an *isolated* trans-stilbene molecule oriented in the transverse direction as in Fig. 1(b) decreases with H_{ee} , thereby exhibiting

the more common behavior. The opposite and surprising behavior in PDPA is a signature of greater electron-hole delocalization in the y -direction for the correlated $1B_u$ than for the uncorrelated $1B_u$. Taken together, these results indicate a synergistic relationship between the confinement in the x -direction and the enhanced delocalization in the y -direction: the delocalization in the y -direction increases the confinement in the x -direction and vice versa.

The larger electron-hole delocalization in the y -direction is an electron correlation effect that can be understood from the natures of the one-electron levels. As shown in Fig. 3(a), the contribution of the backbone chain atoms to the one-electron wavefunction of the highest occupied one-electron level (corresponding to the HOMO of the oligomer in the present context) decreases with t_{\perp} . We have performed similar calculations for all one-electron levels, and for all t_{\perp} , the contribution of the chain atoms to the one-electron wavefunction decreases with increasing energy separation from the chemical potential. Now, for $H_{ee} = 0$, the $1B_u$ is simply the HOMO \rightarrow LUMO transition. For $H_{ee} \neq 0$, the $1B_u$ is a superposition of several transitions, including the HOMO \rightarrow LUMO, HOMO $- 1 \rightarrow$ LUMO $+ 1$, HOMO $- 2 \rightarrow$ LUMO $+ 2$, etc. The y -polarizations of these higher energy excited configurations are larger simply because the wavefunctions themselves have smaller contributions from the chain atoms and larger contributions from the phenyl group atoms, and as consequence the correlated $1B_u$ wavefunction itself has a larger y -character. In Reference 15, we had given a configuration space argument for this electron correlation induced electron-hole delocalization in the y -direction. The present k-space argument is essentially the same explanation, except that the origin of the enhanced delocalization can be understood more quantitatively within these k-space arguments.

As we have already pointed out in section III, increased confinement in the longitudinal direction can in principle raise the energy of the $2A_g$ with respect to the $1B_u$. Although this still needs direct verification, the important point here is that the increased confinement in the x -direction is a consequence of the increased transverse delocalization, which in turn *reduces* the optical gap (see Table I).

TABLE II. The x and y components of $1A_g \rightarrow 1B_u$ transition dipole moments μ_x and μ_y (in Å), as a function of t_{\perp} , for a PDPA oligomer with eight double bonds. Note $t_{\perp} = 0.0$ eV corresponds to an eight double-bond polyene.

t_{\perp}	$H_{ee} = 0$		$H_{ee} \neq 0$ (SCI)	
	μ_x	μ_y	μ_x	μ_y
0.00	3.07	0.35	2.08	0.73
0.35	3.06	0.40	1.97	0.92
0.70	3.04	0.54	1.96	0.99
1.40	3.00	0.97	1.93	1.21
1.80	2.99	1.24	1.91	1.34

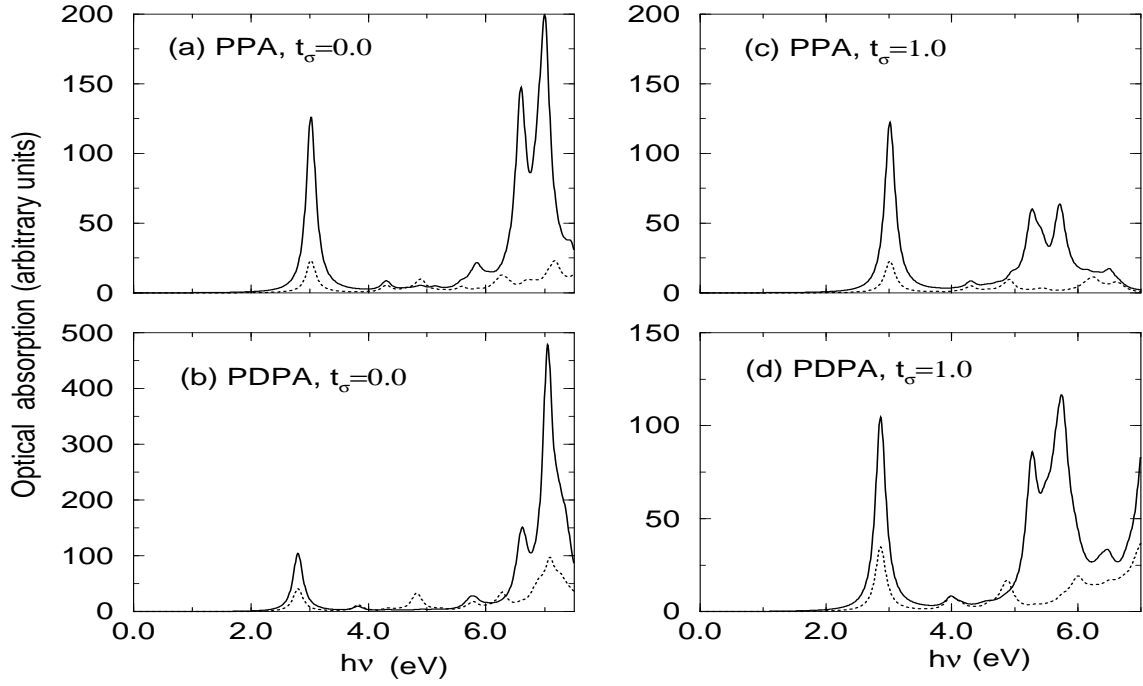


FIG. 5. The calculated x (solid line) and y (dotted lines) components of the optical absorption spectra within the Coulomb correlated model for finite PPA (Figs. (a) and (c)) and PDPA (Figs. (b) and (d)) oligomers with eight double bonds on the backbone polyene chain. Note the different y-axis scales. In all cases $t_{\perp} = 1.4$ eV, while $t_{\sigma} = 0$ in Figs. (a) and (b) and 1.0 eV in Figs. (c) and (d). Coulomb interactions increase the y -character of the lowest absorption and the x -character of the higher energy absorption bands.

B. Overall absorption spectrum

In Figs. 5(a) and (b) we have shown the absorption spectra for PPA and PDPA for the case of nonzero H_{CB} but zero H_{BB} for the specific case of $t_{\perp} = 1.4$ eV. We have included both x - and y -polarizations of the absorption bands in these figures. With nonzero H_{ee} there occur absorption bands at energies as high as 10 eV. These are not included in the Figures. From comparison of these results with the absorption spectra of Figs. 4 (a) and (b), the lowest absorptions in both PPA and PDPA have much larger contributions from the y -component here than for $H_{ee} = 0$, as has already been pointed out in the previous subsection.

There is an even stronger difference between $H_{ee} = 0$ and $H_{ee} \neq 0$ in the high energy region. For $H_{ee} = 0$ the dominant absorption in the high energy region is predominantly y -polarized, although there is also substantial contribution from x -polarized transitions. In contrast, for $H_{ee} \neq 0$, the strong absorption bands centered at ~ 7 eV in both PPA and PDPA in Figs. 5(a) and (b) are not molecular absorptions but primarily charge-transfer chain \rightarrow benzene and benzene \rightarrow chain absorptions which have shifted to high energies because of e-e interaction. The one-electron chain-derived bands are predominantly delocalized along the x -direction (with, however, substantial but smaller y -delocalization) and are also strongly hybridized with the benzene d , d^* MOs. The high energy absorption bands here originate primarily from transitions between these delocalized levels and

the benzene l , l^* MOs, and as discussed in the context of one-electron theory, these transitions are x -polarized.

The charge-transfer type absorptions are redshifted further upon inclusion of H_{BB} , as seen in Figs. 5(c) and (d), where we have shown the optical absorptions for PPA and PDPA, respectively for $t_{\sigma} = 1.0$ eV (note that the y -contribution to the oscillator strength of the lowest energy absorption to the $1B_u$ has remained unchanged, as was claimed in the previous subsection). The redshift of the charge-transfer absorption also occurs within one-electron theory. However, within one-electron theory, there occurs a strong overlap between the x -polarized charge-transfer absorption and the y -polarized molecular absorption (see Fig. 4)(c) and (d)). In contrast, in the energy region of interest, there occurs only strongly x -polarized charge-transfer absorptions, as the molecular absorptions are now strongly blueshifted by e-e interactions. The surprising effect of the e-e interactions is then that the absorption in the relatively high energy region is more strongly x -polarized than the lowest energy absorption, even though the latter is predominantly a backbone chain absorption.

Experimentally, a strong high energy absorption in a PDPA derivative has already been seen by Tada *et al.*,⁹ but this is in an unoriented sample and the polarization characters are unknown. We predict that in oriented samples this absorption will be overwhelmingly x -polarized, which, as seen from comparisons of Figs. 4 and 5, is strictly a correlation effect. In the absence of e-e interaction, the second band should have mixed x and

y -character.

VI. $2A_g$ — $1B_u$ ORDERING

In our earlier Letter, we presented preliminary calculations on the relative ordering of $2A_g$ and $1B_u$ excited states in PDPAs, using selected subsets of MOs of a two double-bond oligomer, within the full-CI (FCI) approach¹⁵. Here we present more sophisticated calculations using all the MOs of oligomers of PDPAs and PPAs with four as well as six backbone carbon atoms, by employing the MRSDCI approach⁴. The MRSDCI is an efficient size-consistent algorithm that has been shown to give energies of the $1B_u$ and the $2A_g$ that are as accurate as the quadruple-CI (QCI) approach for polyenes up to sixteen carbon atoms⁴, and has also been used to determine the frequency dependent nonlinear optical properties of short polyenes³². Note that the PDPA oligomer with six backbone carbon atoms contains 42 carbon atoms altogether, and the Hamiltonian matrices are much larger than those previously investigated. As shown below, strong emphasis was placed on obtaining very high accuracy, and the oligomer with six backbone carbons is the largest that could be investigated without loss of accuracy.

Our calculations are within the rigid bond approximation, i.e., the hopping integrals along the chain are taken to be $t_0(1 \pm \delta)$. We know that enhanced bond alternation can lead to $2A_g$ state being higher than the $1B_u$ state^{5,6}. Therefore, in order to understand the influences of electron correlations and bond alternation on the $2A_g$ - $1B_u$ ordering separately, we considered backbone geometries of PPAs and PDPAs both with standard polyene bond alternation ($\delta = 0.07$), and without any bond alternation ($\delta = 0.0$). For the case of PDPA oligomers, full use of the C_i symmetry of the system was made during the correlated calculations. Therefore, A_g and B_u subspaces were diagonalized in separate calculations³³. However, for the PPA oligomers, because of the lack of any symmetry, A_g and B_u states were obtained by diagonalizing the same Hamiltonian matrix. The $1B_u$ state was identified in this case as the first excited state with large dipole coupling with the ground state. In the MRSDCI calculations presented below, we have ignored H_{BB} , based on our results in Figs. 3, 4 and 5 which clearly indicate that H_{BB} plays an insignificant role in the low energy physics. As far as the phenyl-chain interaction term H_{CB} is concerned, in all the calculations reported below it was parametrized with $t_\perp = 1.4$ eV.

The methodology behind the MRSDCI calculations is as follows. The calculations are initiated with a Hartree-Fock (HF) computation of the ground state of the oligomer concerned, followed by a transformation of the Hamiltonian from the site representation to the HF MO representation. Subsequently, a singles-doubles CI (SDCI) calculation is performed, the three states of in-

terest, viz., the $1A_g$, the $2A_g$, and the $1B_u$ are examined, and the N_{ref} configuration state functions (CSFs) making significant contributions to their many-particle wave functions are identified. The next step is the MRSDCI calculation for which the reference space consists of the N_{ref} CSFs identified in the previous step, and the overall Hamiltonian matrix now includes configurations that are doubly excited with respect to these reference CSFs (thereby including the dominant quadruply excited configurations). The new $1A_g$, $2A_g$, and $1B_u$ states are now re-examined to identify new CSFs contributing significantly to them so as to augment the reference space for the next set of MRSDCI calculations. This procedure is repeated until satisfactory convergence in the excitation energies of the $2A_g$ and $1B_u$ energies is achieved. By the time convergence is achieved typically all CSFs with coefficients of magnitude 0.01 or more in the corresponding many-particle wave functions have been included in the MRSDCI reference space. Naturally, this leads to very large CI matrices, e.g., the dimension of the CI matrix in the MRSDCI calculation on the B_u space of the three unit PDPA oligomer with $N_{ref} = 12$, was ≈ 2.22 millions. The lowest few eigenvalue and eigenvectors of such large matrices were obtained by the Davidson procedure³⁴. The very large N_{ref} required for convergence (even for the $1B_u$) is direct evidence of the contributions by the benzene MOs to the correlated wavefunctions of PPA and PDPA.

The convergence pattern of our MRSDCI calculations with respect to N_{ref} is demonstrated for the case of the PPA oligomer with four backbone carbon atoms in Table III³⁵. These calculations correspond to $\delta = 0$. The $2A_g$ and $1B_u$ excitation energies of various intermediate MRSDCI calculations are measured with respect to the best $1A_g$ ground state obtained in the largest MRSDCI calculation the table ($N_{ref} = 25$). It is for this reason that with increasing N_{ref} , the $2A_g$ and $1B_u$ excitation energies decrease monotonically. It is clear from the behavior of excitation energies with respect to N_{ref} depicted in Table III that by the time the MRSDCI calculation with the largest value of N_{ref} is performed, the $2A_g$ and $1B_u$ excitation energies have converged to an acceptable accuracy.

Our overall MRSDCI results for $2A_g$ and $1B_u$ energies for four and six backbone atom PPA and PDPA oligomers (both with and without bond alternation), along with the corresponding final N_{ref} 's, are summarized in Table IV. In the same Table, for the sake of comparison, the results of full CI calculations on four and six atom polyenes, both with and without bond alternation, are also presented. Upon examining the data presented in Table IV, the following trends emerge: (i) in PDPA oligomers without backbone bond alternation, $1B_u$ and $2A_g$ states are nearly degenerate, while, in the same oligomers with bond alternation, the $1B_u$ state is significantly below the $2A_g$, (ii) in PPA oligomers without bond alternation the $2A_g$ state is below the $1B_u$, while for oligomer geometries with bond alternation $2A_g$

is very slightly above the $1B_u$, (iii) in all cases, the dominant effect of the phenyl-substitution is the lowering of $E(1B_u)$, which decreases as $t\text{-PA} > \text{PPA} > \text{PDPA}$. This last result is in agreement with the SCI results for much longer oligomers in Table I, confirming our statement that the SCI captures the essential nature of the $1B_u$ state.

The occurrence of the $2A_g$ slightly below the $1B_u$ in the PDPA oligomer with $\delta = 0$ and six backbone carbons is not surprising. As discussed in reference 15, exactly as bond-substituted systems can be thought of as effective linear chains with large bond alternation, site-substituted materials can be thought of also as linear chains, but now with composite sites (as opposed to bonds) with small effective on-site Coulomb repulsion U_{eff} . In linear chains of sufficient length, $E(2A_g) < E(1B_u)$ for $\delta = 0$ for any U_{eff} . The more important point, however, is that the energy gap $E(1B_u) - E(2A_g)$ has decreased from 1.15 eV to 0.02 eV in going from the polyene with $\delta = 0$ to the PDPA oligomer. As discussed in section IV.A, the persistence of the Fermi surface degeneracy for $\delta = 0$, even upon phenyl-substitution (see Figs. 2(a) and (b)), ensures that unconditional bond alternation occurs in both PPA and PDPA, and therefore the nonzero δ results in Table IV are more appropriate for the real systems. Although our calculations are for relatively short oligomers, we expect our conclusions regarding the $2A_g$ — $1B_u$ ordering in PDPAs to be valid even for long chains (in particular, for the experimental systems, which are also finite, albeit of length that is twice the lengths studied here). To begin with, the size-dependence of the $2A_g - 1B_u$ energy gap, for the case $E(2A_g) > E(1B_u)$ is steepest at the smallest sizes (a result easily confirmed within one-electron theory). Nevertheless, $E(2A_g) - E(1B_u)$ has almost converged already for the PDPA oligomers with $\delta \neq 0$: for the oligomer with four backbone carbon atoms this energy difference is 0.4 eV, while for the oligomer with six backbone carbons the difference is 0.37 eV. Second, our calculations are for rather large Coulomb interactions and fairly small t_\perp , while in the real systems the Coulomb interactions are perhaps smaller²⁷ and t_\perp might be larger. Finally, it is clear from Table IV that even if the $2A_g$ were to be below the $1B_u$ in short PDPA oligomers, the energy difference would be tiny. Density matrix renormalization group calculations for linear chain systems have suggested that specifically in these cases there is a size-dependent $2A_g - 1B_u$ crossover, where in longer chains $E(2A_g) > E(1B_u)$ again^{36,37}. Thus from all possible considerations, the lowest two-photon state is above the lowest one-photon state in PDPA. In contrast to the PDPA oligomers, $E(2A_g) - E(1B_u)$ has not converged in the PPA oligomers, where this number is 0.13 eV for the oligomer with four backbone carbons and 0.06 eV in the oligomer with six backbone carbons. It is conceivable therefore that in slightly longer oligomers, the $2A_g$ is slightly below the $1B_u$ in PPA.

VII. CONCLUDING DISCUSSIONS

We begin this section with the summary of results obtained in this paper. We agree with the authors of the experimental reference 13 that light emission in PDPAs involves predominantly the backbone chain and not the trans-stilbene moiety. However, as we have shown here, the lowest absorption has a strong y -character, which is enhanced by e-e interactions, and it is this enhanced delocalization in the y -direction that is ultimately the origin of the $2A_g$ occurring above the $1B_u$ in these systems.

TABLE III. Convergence pattern of MRSDCI $2A_g$ and $1B_u$ energies for PPA with four backbone carbon atoms and uniform hopping integrals with respect to increasing N_{ref} . N_{ref} denotes the total number of reference configurations included in the MRSDCI calculation in question. The $2A_g$ and $1B_u$ energies are with respect to the $1A_g$ ground state obtained in the largest calculation ($N_{ref} = 25$). All energies are in eVs.

System	N_{ref}	$E(2A_g)$	$E(1B_u)$
PPA	2	5.50	4.77
	6	4.94	4.69
	8	4.74	4.65
	10	4.67	4.65
	12	4.60	4.63
	15	4.52	4.62
	19	4.50	4.61
	21	4.46	4.60
	23	4.43	4.60
	25	4.42	4.59

TABLE IV. The best MRSDCI results for $2A_g$ and $1B_u$ energies of the oligomers of PDPA and PPA containing four and six carbon atoms along the polyene backbone. Backbone configurations with both $\delta = 0.0$ and $\delta = 0.07$, were considered. For the sake of comparison, the results of the full CI calculations (indicated by FCI in the N_{ref} column) for the two states of the corresponding polyenes are also given. Since for PPA oligomers the A_g and B_u states were obtained in the same calculations, the same values of N_{ref} are indicated for both the A_g and B_u states.

		Energy Gaps (eV)					
		Four backbone carbons			Six backbone carbons		
System	State	N_{ref}	$\delta = 0.0$	$\delta = 0.07$	N_{ref}	$\delta = 0.0$	$\delta = 0.07$
PDPA	$2A_g$	17	4.38	4.98	13	3.62	4.39
	$1B_u$	8	4.25	4.58	12	3.64	4.02
PPA	$2A_g$	25	4.42	5.03	14	3.66	4.47
	$1B_u$	25	4.59	4.90	14	4.02	4.41
polyene	$2A_g$	FCI	4.66	5.35	FCI	3.51	4.37
	$1B_u$	FCI	5.49	5.80	FCI	4.66	5.02

The authors of reference 13 emphasize exciton confinement due to relaxations involving phonons. As shown here, enhanced exciton confinement along the backbone is a consequence of the electron-hole delocalization in the transverse direction. This does not imply that electron-phonon interactions are unimportant. Rather, even if relaxations involving phonons play a strong role in the experimental systems, the $2A_g$ had to be already close to the $1B_u$ in the PDPAs (given the large separation between these in t-PA) due to a purely electronic mechanism, and the present work gives the details of this electronic mechanism. We emphasize that the longitudinal confinement does not necessarily imply enhanced exciton binding energy, as the delocalization in the transverse direction will also reduce the energy of the conduction band threshold. The bond alternation along the backbone decreases with phenyl substitution, also as a direct consequence of smaller chain atom contributions to the one-electron levels at and near the Fermi level. Inclusion of the overlaps between the benzene MOs that occur due to phenyl ring torsions does not change the results of any calculation that probes the low energy photophysics. Finally, we predict a strong second high energy absorption that will be predominantly x -polarized in oriented materials, in contradiction to the prediction of one-electron theory. Experimental work can therefore directly verify the role of e-e interactions.

In the case of PPAs, our results are more difficult to interpret. The convergence behavior of $E(2A_g)$ and $E(1B_u)$ in the two oligomers that have been studied suggests that here $E(2A_g) < E(1B_u)$ in longer chains, although the energy difference can be very small. The small energy difference between these levels would imply that even small perturbations can either reverse this ordering, or lead to strong state mixing. We speculate that the behavior of the PPAs is related to this proximity between the $2A_g$ and the $1B_u$. PPAs with small alkyl groups probably are similar to the PPAs of the same length and are therefore weak emitters. Large alkyl groups either lead to greater main chain bending (and therefore greater exciton confinement) and state reordering, or because of their larger electron donating capability they cause a greater electronic perturbation leading to greater state mixing between the $2A_g$ and the $1B_u$.

In our investigation of optical properties here, we have focused on ground state absorption only, and theoretical studies of excited state absorptions^{11,38} is a topic of future research. In the case of PPP and PPV, it has been claimed that the occurrence of multiple classes of one-electron bands leads to several different photoinduced absorptions in ultrafast pump-probe spectroscopy³⁹, and it is conceivable that similar results will be found here too.

We make one final remark regarding the future application of this work for the design of novel materials. Photo- and electroluminescence of π -conjugated polymers are currently the focus of intense research, and research on the design of novel light emitting diodes using these materials has already reached a mature stage⁴⁰.

Initial work has also shown promising results for laser applications using these materials⁴¹⁻⁴³. In all these cases, however, the materials being used correspond to those obtained by bond substitution, and the optical gaps of such systems are necessarily larger than that of t-PA. Our demonstration that light emission can be a consequence of enhanced delocalization in a direction transverse to the direction of extended conjugation, and that the optical gaps in this latter class of systems are smaller than linear polyenes of the same length, introduces the interesting possibility of designing novel rigid long chain light emitting π -conjugated polymers with optical gaps smaller than that in t-PA. The actual synthesis of rigid materials may be difficult, as the finite conjugation lengths of PPAs and PDPAs already demonstrate, but nevertheless, the present work shows this to be conceptually feasible. Infrared dye lasers are extremely rare, and the possibility of obtaining new light sources at telecommunications wavelengths and in the eye-safe spectral region should make this an exciting new research direction.

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¹ B.S. Hudson, B.E. Kohler and K. Schulten in *Excited States*, Vol. 6, edited by E.C. Lim (Academic, New York, 1982).

² K. Schulten, I. Ohmine and M. Karplus, *J. Chem. Phys.* **64**, 4422 (1976).

³ Z.G. Soos and S. Ramasesha, *Phys. Rev. B* **29**, 5410 (1984).

⁴ P. Tavan and K. Schulten, *Phys. Rev. B* **36**, 4337 (1987).

⁵ Z.G. Soos, S. Etemad, D.S. Galvão and S. Ramasesha, *Chem. Phys. Lett.* **194**, 341 (1992).

⁶ Z.G. Soos, S. Ramasesha, and D.S. Galvão, *Phys. Rev. Lett.* **71**, 1609 (1993).

⁷ The original model of Soos *et al.* for enhanced effective bond alternation is slightly different from this perspective, which, however, is a more pictorial description that can also be justified mathematically. See, Y. Jido, T. Inagaki and H. Fukutome, *Progr. Theor. Phys.* **48**, 808 (1972).

⁸ K. Tada, R. Hidayat, M. Hirohata, M. Teraguchi, T. Masuda and K. Yoshino, *Jpn. J. Appl. Phys.*, part 2 **35**, L1138 (1996).

⁹ K. Tada, R. Hidayat, M. Hirohata, H. Kajii, S. Tatsuhara, A. Fujii, M. Ozaki, M. Teraguchi, T. Masuda and K. Yoshino, *Proc. SPIE-Int. Soc. Opt. Eng.*, **3145**, 171 (1997).

- ¹⁰ A. Fujii, M. Shkunov, Z.V. Vardeny, K. Tada, K. Yoshino, M. Teraguchi and T. Masuda, in reference 9, p. 533.
- ¹¹ I. Gontia, S.V. Frolov, M. Liess, E. Ehrenfreund, Z.V. Vardeny, K. Tada, H. Kajii, R. Hidayat, A. Fujii, K. Yoshino, M. Teraguchi and T. Masuda, Phys. Rev. Lett. **82**, 4058 (1999).
- ¹² R. Sun, Y. Wang, X. Zou, M. Fahlam, Q. Zheng, T. Kobayashi, T. Masuda and A.J. Epstein, Proc. SPIE-Int. Soc. Opt. Eng., **3476**, 332 (1998).
- ¹³ R. Hidayat, S. Tatsuhara, D.W. Kim, M. Ozaki, K. Yoshino, M. Teraguchi and T. Masuda, Phys. Rev. B **61**, 10167 (2000).
- ¹⁴ The phenyl groups themselves may have additional substituted side groups, like n-butyl etc. Thus there exist many different PDPAs, see reference 9. However, the behavior of all these systems are nearly identical, indicating that it is only the conjugation with the bare phenyl groups that modifies the behavior of the phenyl-substituted polyacetylenes.
- ¹⁵ A. Shukla and S. Mazumdar, Phys. Rev. Lett. **83**, 3944 (1999).
- ¹⁶ See, for example, S. Mazumdar and M. Chandross, in *Primary Photoexcitation in Conjugated Polymers: Molecular Exciton versus Band Semiconductor Model*, edited by N. Serdar Sariciftci (World Scientific, Singapore, 1997) pp. 384 – 423, and references therein
- ¹⁷ See, for example, S. Abe in reference 16, pp. 115 – 126, and references therein.
- ¹⁸ M.J. Rice and Yu.N. Gartstein, Phys. Rev. Lett. **73**, 2504 (1994).
- ¹⁹ M. Chandross, S. Mazumdar, M. Liess, P.A. Lane, Z.V. Vardeny, M. Hamaguchi and K. Yoshino, Phys. Rev. B **55**, 1486 (1997).
- ²⁰ D. Comoretto, G. Dellepiane, D. Moses, J. Cornil D.A. dos Santos and J.L. Bredas, Chem Phys. Lett. **289**, 1 (1998).
- ²¹ E.K. Miller, D. Yoshida, C.Y. Yang and A.J. Heeger, Phys. Rev. B **59**, 4661 (1999).
- ²² We are grateful to M.J. Rice for drawing our attention to this interaction.
- ²³ See, for example, *Low Dimensional Conductors and Superconductors*, edited by D. Jerome and L.G. Caron (Plenum, N.Y.) 1987.
- ²⁴ It is not necessary that the actual differences in bond lengths are larger than in polyenes. Even with the same bond lengths it is in principle possible to have larger alternation in the expectation values of the bond order operator, in which case the wave functions have this “built in” information. See J.E. Hirsch in reference 23, pp. 71 – 86.
- ²⁵ B.E. Kohler, J. Chem. Phys. **93**, 5838 (1990).
- ²⁶ K. Ohno, Theor. Chim. Acta **2**, 219 (1964).
- ²⁷ M. Chandross and S. Mazumdar, Phys. Rev. B **55**, 1497 (1997).
- ²⁸ L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (Benjamin, N.Y., 1966).
- ²⁹ J. Cornil, D. Beljonne, R.H. Friend and J.L. Bredas, Chem. Phys. Lett. **223**, 82 (1994).
- ³⁰ W.-P. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. B **22**, 2099 (1980).
- ³¹ M. Chandross, Y. Shimoi and S. Mazumdar, Phys. Rev. B **59**, 4822 (1999).
- ³² Z. Shuai, D. Beljonne and J.L. Bredas, J. Chem. Phys. **97**, 1132 (1992).
- ³³ The C_i group has two irreducible representations: A_g and A_u . The two-photon states in this group belong to the A_g representation, while the one-photon states belong to A_u representation. However, in the present paper we refer to the one-photon states of PDPAs as the B_u states in order to facilitate direct comparison to the similar states in polyenes.
- ³⁴ E.R. Davidson, J. Comp. Phys. **17**, 87 (1975).
- ³⁵ In this small molecule the $1B_u$ and the $2A_g$ energies are rather high and therefore close to the $d \rightarrow l^*$ and $l \rightarrow d^*$ excitations of the phenyl segments. However, from transition dipole couplings and the natures of the configurations that form the many-body wavefunctions the identifications of the $1B_u$ and the $2A_g$ are simple and unambiguous.
- ³⁶ Z. Shuai, J.L. Bredas, S.K. Pati and S. Ramasesha, Phys. Rev. B **56**, 9298 (1997).
- ³⁷ R.J. Bursill and W. Barford, Phys. Rev. Lett. **82**, 1514 (1999).
- ³⁸ T.L. Gustafson, E.M. Kylo, T.L. Frost, R.G. Sun, H. Lim, D.K. wang, A.J. Epstein, C. Lefumeux, G. Brudzinski, G. Buntinx and O. Poizat, Synth. Metals, in press (2000).
- ³⁹ A. Chakrabarti and S. Mazumdar, Phys. Rev. B **59**, 4839 (1999).
- ⁴⁰ R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. dos Santos, J.L. Bredas, M. Lögdlund and W.R. Salaneck, Nature **397**, 121 (1999) and references therein.
- ⁴¹ N. Tessler, G.J. Denton and R.H. Friend, Nature (London) **382**, 695 (1996).
- ⁴² F. Hide, M.A. Diaz-Garcia, B.J. Schwartz, M.R. Andersson, Q. Pei and A.J. Heeger, Science **273**, 1833 (1996).
- ⁴³ S.V. Frolov, W. Gellermann, M. Ozaki, K. Yoshino and Z.V. Vardeny, Phys. Rev. Lett. **78**, 729 (1997).